Faculty of Engineering

MODELLING AND OPTIMIZATION OF ANTIBACTERIAL COMPOSITE MEMBRANE BY USING BOX-BEHNKEN

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MODELLING AND OPTIMIZATION OF ANTIBACTERIAL COMPOSITE MEMBRANE BY USING BOX-BEHNKEN

SITI NUR SHAFINA BT SABARUDDIN

A dissertation submitted in partial fulfillment

of the requirement for the degree of

Bachelor of Engineering with Honours

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Dedicated to my beloved parents and my family who always bestow me sustainable motivations and encouragements

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ABSTRACT

The main objective of this is research is to develop a regression model and to optimize the performance of antibacterial composite membrane. The parameters that are to be optimized are the concentration of antibacterial additives, the composition of solvent/non-solvent system in the casting solution and the composition of coagulation bath. The concentration of silver nitrate ($AgNO_3$) as antibacterial additives was varied between 1.0 g to 2.0 g, while the percentage of N-methyl-2-pyrrolidone (NMP) as the solvent in the casting solution is varied from 90wt% to 100wt%. The percentage of ethanol in the coagulation bath was varied from 0wt% to 25wt%. The Design of Experiment (DoE) was conducted by using 3-factorial 3-level Box-Behnken. The performance of the membranes fabricated were evaluated in terms of membrane flux and antibacterial activity in term of *E. coli* inhibition, which served as the responses for the modelling and optimization purposes. The modelling and optimization process were conducted by using Response Surface Methodology (RSM). The resultant equations showed R^2 values of 0.9003 and 0.9789 for the membrane water flux and *E. coli* inhibition respectively. The analysis of variance (ANOVA) proved that both models were significant. Based on the results, it was observed that weight percentage of NMP in casting solution and weight of $AgNO_3$ added had significant impact on the membrane water flux and *E. coli* inhibition. Optimum values of parameters for preparation of antibacterial composite membrane were obtained using multiple response method for 70% *E. coli* inhibition as target value. Based on the optimization results, the best membrane water flux, which was 19.49 L/m^{2}h, was obtained at weight percentage of NMP in casting solution of 95.61%, weight percentage of ethanol in coagulation bath, and weight of $AgNO_3$ of 1.26 g, with desirability of 1.

Keywords; Optimization, antibacterial, silver nitrate, NMP, Box-Behken, Response Surface Methodology

ABSTRAK

Objektif utama kajian ini adalah untuk membina sebuah model dan untuk mengoptimumkan prestasi membran komposit anti-bakteria. Parameter yang akan dioptimumkan adalah kandungan aditif antibakteria, komposisi sistem pelarut-bukan pelarut dalam larutan acuan, dan komposisi larutan pembekuan. Kandungan perak nitrat ($AgNO_3$) sebagai aditif anti-bakteria dibezakan antara 1.0g dan 2.0 g, sementara peratusan N-methyl-2-pyrrolidone (NMP) sebagai pelarut dibezakan dari 90 berat% sehingga 100 berat%. Peratusan etanol dalam larutan pembekuan dibezakan dri 0 berat% sehingga 25 berat%. Reka Bentuk Experimen dilakukan dengan menggunakan teknik 3-faktor 3-level Box-Behnken. Prestasi membrane yang telah direka diuji dari segi fluks membran dan aktiviti anti-bakteria dari segi perencatan *E. coli*, yang juga merangkap sebagai respon untuk tujuan pembinaan model dan proses pengoptimuman. Proses pembinaan model dan optimasi dilakukan dengan menggunakan Kaedah Tindak Balas Permukaan. Persamaan yang diperolehi menunjukkan nilai R^2 0.9003 untuk model fluks membran dan 0.9789 untuk model perencatan *E. coli*. Berdasarkan keputuan yang diperolehi, peratusan NMP sebagai pelarut dan berat $AgNO_3$ memberi impak yang besar kepada fluks membrane dan perencatan *E. coli*. Nilai optimum untuk parameter-parameter yang diperlukan untuk penyediaan membrane komposit anti-bakteria didapati dengan menggunakan teknik pelbagai respons untuk nilai perencatan *E. coli* 70%. Keputasan pengoptimuman mendapati fluks membrane terbaik diperolehi pada berat peratusan NMP sebagai larutan 96.61%, berat peratusan etanol dalam larutan pembekuan 6.48% dan berat $AgNO_3$ 1.26g.

Kata kunci: Pengoptimuman, anti-bakteria, perak nitrat, NMP, Box-Behnken, Tindak Balas Permukaan

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ABBREVIATIONS

AgCl	-	Silver chloride
$AgNO_3$	-	Silver nitrate
AgNP	-	Silver nanoparticle
ANOVA	-	Analysis of variance
DoE	-	Design of Experiment
FTIR	-	Fourier transfer infrared spectroscopy
ICP-MS	-	Inductively coupled plasma mass spectrometry
MWCNT	-	Multiwall carbon nanotube
NMP	-	N-methyl-2-pyrrolidone
PDA	-	Polydopamine
PEM	-	Polyelectrolytes multilayer
PES	-	Polyethersulfone
PSf	-	Polysulfone
PVA	-	Polyvinyl alcohol
PVDF	-	Polyvinylidene fluoride
RO	-	Reverse osmosis
ROS	-	Reactive oxidation species
RSM	-	Response surface methodology
SEM	-	Scanning electron microscopy
SH	-	Sulfhydryl
UF		Ultrafiltration
WTP		Water treatment plant

NOMENCLATURES

℃	-	Degree Celcius
CFU/ml	-	Colony-forming unit/ milliliter
cm	-	Centimeter
Da	-	Dalton
g	-	Gram
L/cap.day	-	Liter per capacity per day
L/m^2.h.bar	-	Liter per meter square. hour. bar
ml	-	Milliliter
MLD	-	Million liter per day
mm	-	Millimeter
nm	-	Nanometer
ppm	-	Parts per million
s	-	Second
wt%	-	Weight percent

CHAPTER 1

INTRODUCTION

1.1 Introduction

In many field of studies, data description and analysis is conducted by developing mathematical models. Mathematical models help in making valid inferences that can be used in latter stages of the study. Validation of models can be achieved by using optimization techniques. Basically, optimization techniques are used to specify the model, before estimating the model parameters and the subsequently validating the model (Rustagi, 1994). There are many optimization techniques that can be used to validate a mathematical model. For multi-objective optimizations, the techniques include Taguchi method, Monte Carlo methods and Response Surface Methodology (RSM). According to Madić et al. (2014), the main aim of Taguchi method is to determine the optimum operating conditions so that the performance variability and deviation from the target value of interest can be minimized. This method is widely used in manufacturing practice due to its ability to come up with results that are robust with respect to all various causes of variation, as well as the simplicity of the optimization procedures. Monte Carlo methods, on the other hand, is more popular in financial field as well computer science, though the general application is also used in various aspects of engineering. The methods consist of algorithms that are capable to solve a variety of computational problems by using random numbers, and are specifically useful for problems that comprised of many degree of freedom (Amar, 2006).

This research will focus on RSM as the optimization technique. RSM is a compilation of mathematical and statistical techniques used to construct empirical model. The RSM mainly aim to optimize the output variable, or response, which is influenced by a number of input variables, also known as independent variable, by conducting a series of tests (runs) called experiments that of specific designs (Mokshedi & Akbarian, 2014). RSM employs several design methods based on the required levels of analysis. According to Cavazzuti (2013), among design of experiments that are used for optimization application are randomized complete block design (RCBD), which focus on one specific factor as a primary factor, Latin square design, which aims to reduce the number of samples required without affecting the primary factor, full factorial design, which uses the available data efficiently without confounding the effects of the parameters, fractional factorial design, which runs only a subset of a full factorial, central composite design (CCD), which is a 2^k full factorial design added with central point and a star point, and Box-Behnken design, which is an incomplete 3-level factorial design, constructed to limit the sample size as the number of parameters increase.

The design of experiment (DOE) chosen for this research is Box-Behnken design which is one of the RSM 3-levels experiment designs. The design was developed by Box and Behnken, and it provides three levels of each factors that are to be analysed as well as consists of a particular subset of the factorial combination from the 3*k* factorial design (Khuri & Mukhopadhyay, 2010). **Figure 1.1** shows the Box-Behnken design for three-variable optimization with its 13 experimental points. Box-Behnken design is widely used in industrial research due to its economical design, in which three levels suffice for each factor, the settings denoted by -1, 0, 1 (Khuli & Mukhopadhyay, 2010).

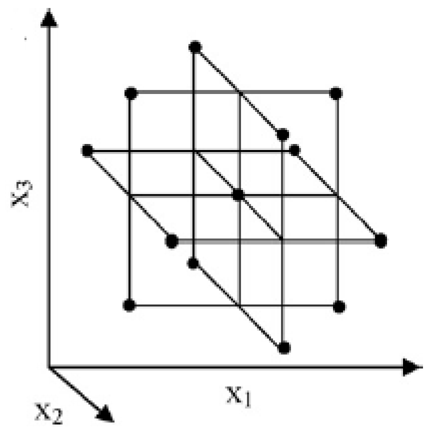

Figure 1.1 Box-Behnken design for three-variable optimization

(Bezerra et al., 2008)

Some examples of application of Box-Behnken designs in analytical chemistry field are optimization of the chiral separation of drugs, optimizing a microwave-assisted extraction method for the extraction of persistent pesticides, optimizing a flow injection system for the on-line pre-concentration of heavy metal using silica gel functionalized with methylthiosalicylate and optimization the chromatographic determination of captopril (Bezerra et al., 2008).

With the increase of functionality of membrane technology, many researches have been conducted to optimize the membrane with the objective of to improve the membrane performance in field the applications. The parameters that are optimized must have significant impacts to the desired function or purpose of the membrane. Among common parameters to be optimized are the concentration of the polymer, the concentration of the cross-linking agent and the concentration of the nanoparticles. The optimized models are validated by measuring the response which are usually in terms of permeate flux and removal or rejection efficiency. **Table 1.1** shows several membrane optimizations that have been covered in various previous studies.

Table 1.1 Membrane optimizations in previous studies

Type of membrane	**Parameters studied**	**Response**	**Reference**
PVDF hollow fibre (direct contact membrane distillation for water desalination)	1. Inlet temperature of feed and permeate 2. Flow velocity of feed solution 3. Module packing density 4. Length-diameter ratio of module	1. Average permeate flux 2. Water productivity per unit volume of module 3. Water production per unit energy consumption	(Cheng et al., 2016)
PVA/PES composite membrane	1. PVA concentration 2. Glutaraldehyde concentration as cross-linking agent 3. TiO_2 nanoparticles concentration as membrane surface and performance modifier	1. Permeate flux 2. COD	(Pourjafar, 2012)
Mesoporous silica nanoparticle (mMSN)/polyamide thin film nanocomposite	1. Concentration of mMSN	1. Water flux 2. Rejection to Na_2SO_4	(Wu et al., 2013)
Polyamide thin film composite membrane for organic solvent nanofiltration	1. Trimesoyl chloride (TMC) concentration 2. M-phenylenediamine (MPD) concentration	1. Fit oil rejection 2. Permeate flux	(Namvar-Mahboub, Pakizeh, 2013)

	3. Support immersion time in organic solution 4. Support immersion time in aqueous solution 5. Curing temperature		
Thin film composite membrane for water desalination	1. Casting thickness 2. Polysulfone (PSf) concentration 3. M-phenylenediamine soaking time 4. Curing time 5. Curing temperature 6. Interfacial polymerization	1. Permeate flux 2. Rejection rate	(Namaghi et al., 2015)
PES mixed matrix nanofiltration membrane embedded with polymer wrapped MWCNT	1. Concentration of dye solution 2. pH of dye solution 3. Membrane polymer composition	1. Permeate flux 2. Dye removal efficiency	(Ghaemi et al., 2015)

The focus of this research is optimization of antibacterial membranes. Antibacterial properties can be embedded to a membrane by some modification on the membrane surface, usually by embedding the surface with nanoparticles with antibacterial properties. Examples of nanomaterials with antibacterial properties are silver, copper, titanium oxide nanoparticles, graphene oxide and enzymes (Park et al., 2016). According to Park et al. (2016) and Huang et al. (2015), the silver nanoparticles has been extensively explored as compared to other agents due to their high biocidal effect in broad spectrum while not causing any harm to human. According to a study conducted by Jung et al. (2008), over 5 $\log_{10}$ CFU/ml of total number of *S. auereus* bacteria was reduced after being treated with silver ion solution (0.2 ppm) for 90 minutes, while the *E. coli* bacterial count decreases from 10^5 CFU/ml to less than 20 CFU/ml within 30 minutes at silver ion concentration of 0.2 ppm. It has been claimed in previous studies that silver ions are capable to bind to the sulphur functional groups, destabilizing proteins and enzymes responsible for transport and metabolic pathway, besides generating reactive oxidation species (ROS) that attack proteins and cause permanent damage to the structure and the function of DNA molecules, as well as forming pits and holes on the cellular surface with direct interaction between bacteria cells and the silver nanoparticles, resorting to cellular membrane destabilization, cytoplasmic material leak and morphological integrity loss (Andrade et al., 2015).

Many researches have been conducted on the methods of membrane surface modification to improve the membrane performance as well as embedding anti-fouling or anti-microbial properties to the membranes. Park et. al., (2016) listed several conventional membrane surface modification methods as physical adsorption, covalent binding, layer-by-layer coating and in-situ incorporation. In their study, Tang et al. (2015) has included several cases of membrane surface modification by assembly of polyelectrolyte multilayers (PEMs) on membrane surface via later-by-later adsorption to inhibit biofouling. Among the cases are modification of polyethersulfone (PES) membranes with PEMs comprising 1.5 bilayers of poly(styrene sulfonate)(PSS) and poly(diallyldimethylammonium chloride) (PDADMAC), modification of polymide thin-film composite (TFC) RO membranes with 10 bilayers of polyethylene amine (PEI) and poly(acrylic acid) (PAA) and modification of polysulfone (PSU) membranes with 2 bilayers of poly(allylamine hydrochloride)(PAH) and PAA. According to Huang et al. (2015), several methods can be used to enhance the hydrophilicity and antifouling property of membrane. These methods include surface coating and chemical grafting. Biofouling problems, on the other hand, are overcame by methods such as direct incorporation of silver nanoparticles (AgNPs) into the casting solution of the polymer, AgNPs deposition by directly reducing 3_3 on thin film composite (TFC) reverse osmosis composite membrane, and covalent immobilization of colloidal AgNPs onto PVDF membrane, in which a thiol-end functional amphiphilic block copolymer linker functions as an intermediate. These methods have disadvantages in terms of AgNPs leach-out, water permeability reduction and complicated process. Park et al. (2016) has proposed a new technique to incorporate AgNPs onto commercially available TFC RO membrane by using arc plasma deposition(APD). APD is a physical vapor deposition technique, in which a metal cathode generates arc pulse plasma to release highly ionized metal ions which will then deposited on a substrate with high kinetic energy to be condensed to nanoparticles. Another new method proposed by Huang et al. (2015) is in-situ immobilization of AgNPs, which is by depositing polydopamine (PDA) layer on commercial PSf ultrafiltration (UF) before the AgNPs are immobilized on the PDA-coated membrane through in situ reduction of silver ammonia aqueous solution ($Ag(NH_3)_2OH$), as shown in **Figure 1.2**.

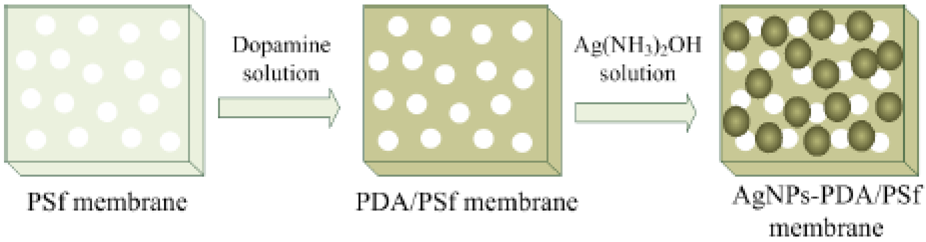

Figure 1.2: Surface modification with self-polymerized dopamine and in-situ immobilization of AgNPs to form AgNPs-PDA/PSf membrane (Huang et al., 2015)

In this research, an experiment design for parameters concerning composite silver nitrate ($AgNO_3$) will be developed by using Box-Behnken and subsequently a model for the membrane will be developed. The model will be optimized by using RSM.

1.2 Problem Statement

The disinfection step by chlorination in conventional water treatment may affect the water quality negatively with the formation of carcinogenic by-products which requires more steps to be removed (Ang et al., 2015). The usage of antibacterial membrane as disinfection method can overcome this problem. In order to ensure efficient disinfection process, the antibacterial performance of the nanomaterials or agents must be maximized by manipulating the composition of the anti-bacterial agent incorporated on the membrane and other parameters. The fabrication of membranes without any guidelines must be conducted by trial-and-error basis, thus is costly and time consuming. The costs involved include the cost for the materials of the membranes as well as the cost of the nanoparticles that are to be embedded on the surface of the membrane for properties modification. Composite membranes that consist of multiple materials are especially relatively costlier to fabricate due to the higher number of materials needed. Therefore, it is more feasible to develop a model concerning the decided parameters and subsequently, optimizing the model before the membrane is fabricated. According to Bezerra et al. (2008), optimization can be defined as improving the performances of a system, a process or a product with an aim to acquire the maximum benefit from it, and from an analytical chemistry view, a way to discover the conditions to be applied to a procedure for the best possible response to be produces. Thus, it can be expected that the membrane fabricated by using the optimized model will show the best result for application.